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(54) Electron transporting materials for organic electroluminescent devices

Elektrotransportmittelmaterialien für organische elektrolumineszente Vorrichtungen

Matériau transportant des électrons pour dispositifs organiques électroluminescents

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(56) References cited:

US-A- 3 673 202 US-A- 4 263 441
US-A- 4 539 507 US-A- 5 298 189
US-A- 5 536 588

- REISER A ET AL: "Fluorescence of aromatic benzoxazole derivatives" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 5 APRIL 1972, USA, vol. 94, no. 7, ISSN 0002-7863, pages 2414-2421, XP002063807
- DATABASE WPI Section Ch, Week 9533 Derwent Publications Ltd., London, GB; Class E13, AN 95-252263 XP002063808 & JP 07 157 473 A (CHISSO CORP), 20 June 1995
- PATENT ABSTRACTS OF JAPAN vol. 018, no. 686 (C-1292), 26 December 1994 & JP 06 271844 A (TOYO INK MFG CO LTD), 27 September 1994,
- PATENT ABSTRACTS OF JAPAN vol. 096, no. 003, 28 March 1996 & JP 07 310071 A (KONICA CORP), 26 November 1995,

EP 0 825 803 B1

Description

[0001] This invention relates to organic electroluminescent (EL) devices. More specifically, this invention relates to the use of a class of organic materials for the electron-transport layer in a multi-layer organic EL device.

[0002] Organic EL devices are known to be highly efficient and are capable of producing a wide range of colors. Useful applications such as flat-panel displays have been contemplated. Representative of earlier organic EL devices are US-A-3,172,862, US-A-3,173,050, Dresner, "Double Injection Electroluminescence in Anthracene," RCA Review, Vol. 30, pp. 323-334, 1969; and US-A-3,710,167. Typical organic emitting materials were formed from a conjugated organic host material and a conjugated organic activating agent having condensed benzene rings. Naphthalene, anthracene, phenanthrene, pyrene, benzopyrene, chrysene, picene, carbazole, fluorene, biphenyl, terphenyls, quarterphenyls, triphenylene oxide, dihalobiphenyl, trans-stilbene, and 1,4-diphenylbutadiene were offered as examples of organic host materials. Anthracene, tetracene, and pentacene were named as examples of activating agents. The organic emitting material was present as a single layer medium having a thickness much above 1 micrometer. Thus, this organic EL medium was highly resistive and the EL device required a relatively high voltage (>100 volts) to operate.

[0003] The most recent discoveries in the art of organic EL device construction have resulted in devices having the organic EL medium consisting of extremely thin layers (<1.0 micrometer in combined thickness) separating the anode and cathode. Herein, the organic EL medium is defined as the organic composition between the anode and cathode electrodes. In a basic two-layer EL device structure, one organic layer is specifically chosen to inject and transport holes and the other organic layer is specifically chosen to inject and transport electrons. The interface between the two layers provides an efficient site for the recombination of the injected hole-electron pair and resultant electroluminescence. The extremely thin organic EL medium offers reduced resistance, permitting higher current densities for a given level of electrical bias voltage. Since light emission is directly related to current density through the organic EL medium, the thin layers coupled with increased charge injection and transport efficiencies have allowed acceptable light emission levels (for example brightness levels capable of being visually detected in ambient light) to be achieved with low applied voltages in ranges compatible with integrated circuit drivers, such as field effect transistors.

[0004] Further improvement in organic EL devices such as color, stability, efficiency and fabrication methods have been disclosed in US-A-4,356,429; US-A-4,539,507; US-A-4,720,432; US-A-4,865,211; US-A-5,151,629; US-A-5,150,008; US-A-5,141,671; US-A-5,073,446; US-A-5,061,569; US-A-5,059,882; US-A-5,059,881; US-A-5,047,867; US-A-4,950,950; US-A-4,769,292; US-A-5,104,740; US-A-5,227,252; US-A-5,256,945; US-A-5,069,975; and US-A-5,122,711; US-A-5,366,811; US-A-5,126,214; US-A-5,142,343; US-A-5,389,444; US-A-5,458,977.

[0005] For the production of full-color EL display panel, it is necessary to have efficient red, green and blue (RGB) EL materials. With these primary materials, an appropriate combination of their emissions will generate any desirable EL hues or colors, including white. Especially important is the production of blue EL materials, because, given an efficient blue EL material, it is possible to produce other EL colors by a downhill energy transfer process. For instance, a green EL emission can be obtained by doping into a host blue EL material with a small amount of a green fluorescent sensitizing dye. This host-guest energy transfer scheme has been discussed in US-A-4,769,292. Similarly, a red EL color can be produced by doping the blue EL host material with a red fluorescent dye. In a somewhat analogous scheme, the fluorescent sensitizing dye may be placed outside the blue EL emitter to effect a shift in the EL emission wavelengths, as discussed in US-A-5,015,999. In this scheme, the sensitizing medium absorbs the blue photon generated by the blue EL emitter, which then emits at longer wavelengths.

[0006] US-A-4 539 507 describes an EL device comprising an optical brightener which can be a 4,4'-bis(2-benzoxazolyl) compound.

[0007] US-A-5 536 888 describes an EL element using an benzoxazole derivative (example 3).

[0008] JP-07 310 071 describes an EL element using a compound which comprise two benzoxazole, benzothiazole or benzimidazole radicals.

[0009] JP 07 157 473 describes an EL element using a compound having three benzoxazole, benzothiazole or benzimidazole linked by a 1,3,5-triazine moiety.

[0010] Co-pending application EP97202458, filed on 08.08.1997, claiming a priority of 20.08.1996 and published EP825804 on 25.02.1998 describes electroluminescent devices having at least one luminescent medium comprising organic compounds substituted with 3 to 8 benzazole moieties.

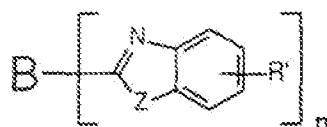
[0011] It has been discovered that a class of novel organic materials known as benzazoles is capable of producing highly efficient EL devices. In particular, the benzazoles are found to produce blue electroluminescence when they are used directly as the emitting layer in a multi-layer EL device. It has been discovered that the benzazoles are capable of transporting electrons efficiently and therefore they can be used advantageously as the electron-transport layer in conjunction with other emissive materials in a multi-layer EL device.

[0012] The present invention provides a wide bandgap electron-transport material useful for organic EL devices;

the organic EL devices comprising an anode, a cathode, and an organic EL medium between the anode and the

cathode;

the EL medium contains an electron-transport layer; the electron-transport layer contains a benzazole compound of molecular formula (1):



(1)

Formula I

wherein:

n is an integer of from 3 to 6;

Z is NR or S; and

R and R' are individually hydrogen; alkyl of from 1 to 24 carbon atoms, for example, propyl, t-butyl, heptyl, and the like; aryl or hetero-atom substituted aryl of from 5 to 20 carbon atoms, for example, phenyl and naphthyl, furyl, thiienyl, pyridyl, quinolinyl and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring;

S is a linkage unit consisting of alky, aryl, substituted alky, or substituted aryl which conjugately or unconjugately connects the multiple benzazoles together.

[0013] These and other advantages of this invention can be better appreciated by reference to the following detailed description considered in conjunction with the drawings in which:

Figs. 1, 2, and 3 are schematic diagrams of the multi-layer structures of preferred EL devices of this invention.

Fig. 4 shows the spectral characteristic of an EL device described in example 3.

[0014] An EL device 100 according to the invention is schematically illustrated in Fig. 1. The support is layer 102 which is an electrically insulating and optically transparent material such as glass or plastic. Anode 104 is separated from cathode 106 by an organic EL medium 108, which, as shown, consists of two superimposed layers of organic thin films. Layer 110 located on the anode forms a hole-transport layer of the organic EL medium. Located above the hole-transport layer is layer 112, which forms an electron-transport layer of the organic EL medium. The anode and the cathode are connected to an external AC or DC power source 114 by conductors 116 and 118, respectively. The power source can be pulsed, periodic, or continuous.

[0015] In operation, the EL device can be viewed as a diode which is forward biased when the anode is at a higher potential than the cathode. Under these conditions, holes (positive charge carriers) are injected from the anode into the hole-transport layer, and electrons are injected into the electron-transport layer. The injected holes and electrons each migrate toward the oppositely charged electrode, as shown by the arrows 120 and 122, respectively. This results in hole-electron recombination and a release of energy in part as light, thus producing electroluminescence.

[0016] The region where the hole and electron recombine is known as the recombination zone. The two-layer device structure is designed specifically to confine the recombination at the vicinity near the interface between the hole-transport and the electron-transport layers where the probability for producing electroluminescence is the highest. This recombination confinement scheme has been disclosed by Tang and Van Slyke [Applied Physics Letters, Volume 51, Page 913, 1987] and is done by choosing carrier injecting electrodes of suitable work-functions and transport materials of a proper carrier mobility. Away from this interface between the organic layers and in particular at or near the injecting electrodes, the recombination of hole and electron would generally be much less radiative due to the effect of radiative quenching by a conducting surface.

[0017] Organic EL device 200 shown in Fig. 2 is illustrative of another preferred embodiment of the invention. The insulating and transparent support is layer 202. The anode 204 is separated from the cathode 206 by an EL medium 208, which, as shown, consists of three superimposed layers of organic thin films. Layer 210 adjacent to anode 204 is the hole-transport layer. Layer 214 adjacent to cathode 206 is the electron-transport layer. Layer 212 which is a

between the hole-transport layer and the electron transport layer is the luminescent layer. This luminescent layer also serves as the recombination layer where the hole and electron recombines.

[0018] The configurations of devices 100 and 200 are similar, except that an additional luminescent layer is introduced in device 200 to function primarily as the site for hole-electron recombination and thus electroluminescence. In this respect, the functions of the individual organic layers are distinct and can therefore be optimized independently. Thus, the luminescent or recombination layer can be chosen to have a desirable EL color as well as a high luminance efficiency. Likewise, the electron and hole transport layers can be optimized primarily for the carrier transport property.

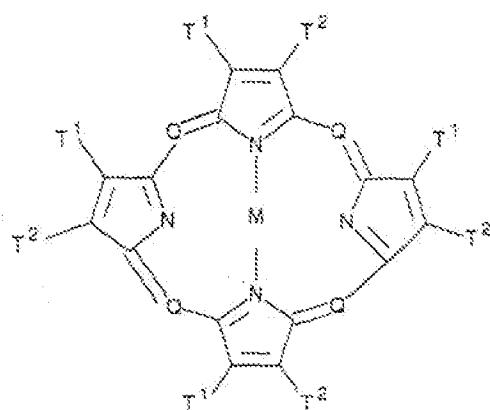
[0019] Organic device 300 is illustrative of yet another preferred embodiment of the present invention. The insulating and transparent support is layer 302. The anode 304 is separated from the cathode 306 by an EL medium 308, which, as shown, consists of five superimposed layers of organic thin films. Located on top of the anode layer 304 are, in sequence, the hole-injection layer 310, the hole-transport layer 312, the luminescent layer 314, the electron-transport layer 316, and the electron-injection layer 318. The structure of device 300 is similar to device 200, except that a hole-injection layer and an electron injection layers are added to improve the injection efficiency of the respective anode and cathode. It is understood that an EL device may be constructed having either the hole or electron injection layer present in the organic EL medium without unduly compromising the device performance.

[0020] The substrate for the EL devices 100, 200, and 300 is electrically insulating and light transparent. The light transparent property is desirable for viewing the EL emission through the substrate. For applications where the EL emission is viewed through the top electrode, the transmissive characteristic of the support is immaterial, and therefore any appropriate substrate such as opaque semiconductor and ceramic wafers can be used. Of course, it is necessary to provide in these device configurations a light transparent top electrode.

[0021] The composition of the organic EL medium is described as follows, with particular reference to device structure 300.

[0022] A layer containing a porphyrinic compound forms the hole injecting layer [Layer 310 of Fig. 3] of the organic EL device. A porphyrinic compound is any compound, natural or synthetic, which is derived from or includes a porphyrin structure, including porphine itself. Any of the prophyrinic compounds disclosed in US-A-3,936,031 or US-A-4,356,429, can be employed.

[0023] Preferred porphyrinic compounds are those of structural formula (II):



(II)

50 wherein

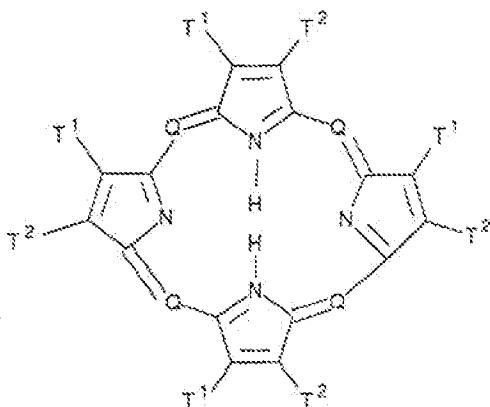
Q is —N= or —C(R)=;

M is a metal, metal oxide, or metal halide;

R is hydrogen, alkyl, aralkyl, aryl, or alkaryl; and

55 T¹ and T² represent hydrogen or together complete a unsaturated six member ring, which can include substituents, such as alkyl or halogen. Preferred six membered rings are those formed of carbon, sulfur, and nitrogen ring atoms. Preferred alkyl moieties contain from about 1 to 6 carbon atoms while phenyl constitutes a preferred aryl moiety.

[0024] In an alternative preferred form the porphyrinic compounds differ from those of structural formula (I) by substitution of two hydrogens for the metal atom, as indicated by formula (III):



(III)

[0025] Highly preferred examples of useful porphyrinic compounds are metal free phthalocyanines and metal containing phthalocyanines. While the porphyrinic compounds in general and the phthalocyanines in particular can contain any metal, the metal preferably has a positive valence of two or higher. Exemplary preferred metals are cobalt, magnesium, zinc, palladium, nickel, and, particularly, copper, lead, and platinum.

[0026] Illustrative of useful porphyrinic compounds are the following:

Porphine
1,10,15,20-tetraphenyl-21H,23H-porphine copper (II)
1,10,15,20-tetraphenyl-21H,23H-porphine zinc (II)

Copper phthalocyanine

Chromium phthalocyanine fluoride

[0027] The hole transporting layer [312] of the organic EL device contains at least one hole transporting aromatic tertiary amine, where the latter is understood to be a compound containing at least one trivalent nitrogen atom that is bonded only to carbon atoms, at least one of which is a member of an aromatic ring. In one form the aromatic tertiary amine can be an arylamine, such as a monarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylamines are illustrated in US-A-3,180,730. Other suitable triarylamines substituted with vinyl or vinyl radicals and/or containing at least one active hydrogen containing group are disclosed in US-A-3,587,450 and US-A-3,658,520.

[0028] Another class of aromatic tertiary amines are those which include at least two aromatic tertiary amine moieties. Such compounds include those represented by structural formula (IV).

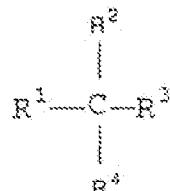


(IV)

wherein

Q^1 and Q^2 are independently aromatic tertiary amine moieties and
 G is a linking group such as an arylene, cycloalkylene, or alkylene group of a carbon to carbon bond.

[0029] A preferred class of triarylamines satisfying structural formula (IV) and containing two triarylamine moieties are those satisfying structural formula (V):



(V)

where

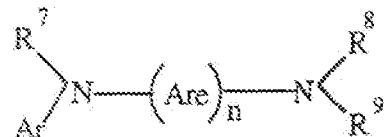
R^1 and R^2 each independently represents a hydrogen atom, an aryl group, or an alkyl group or R^1 and R^2 together represent the atoms completing a cycloalkyl group and
 R^3 and R^4 each independently represents an aryl group which is in turn substituted with a diaryl substituted amino group, as indicated by structural formula (VI):



(VI)

wherein R^5 , R^6 are independently selected aryl groups.

[0030] Another preferred class of aromatic tertiary amines are tetraaryldiamines. Preferred tetraaryldiamines include two diarylamine groups, such as indicated by formula (VII), linked through an arylene group:



(VII)

wherein

Are is an arylene group,
 n is an integer of from 1 to 4, and

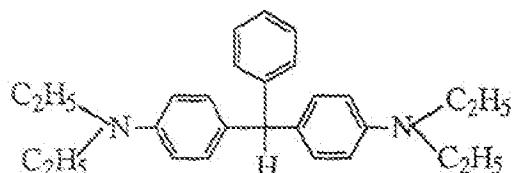
Ar, R⁷, R⁸, and R⁹ are independently selected aryl groups.

[0031] The various alkyl, alkylene, aryl, and arylene moieties of the foregoing structural formulae (IV), (V), (VII), can each in turn be substituted. Typical substituents including alkyl groups, alkoxy groups, aryl groups, aryloxy groups, and halogen such as fluoride, chloride, and bromide. The various alkyl and alkylene moieties typically contain from about 1 to 8 carbon atoms. The cycloalkyl moieties can contain from 3 to about 10 carbon atoms, but typically contain five, six, or seven ring carbon atoms-for example, cyclopentyl, cyclohexyl, and cycloheptyl ring structures. The aryl and arylene moieties are preferably phenyl and phenylene moieties.

[0032] Illustrative of useful hole transport compounds are the following:

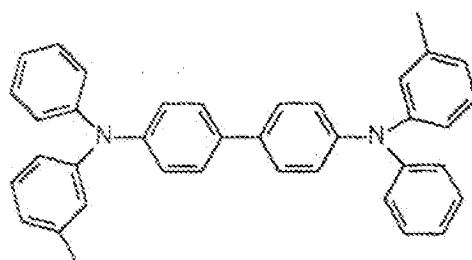
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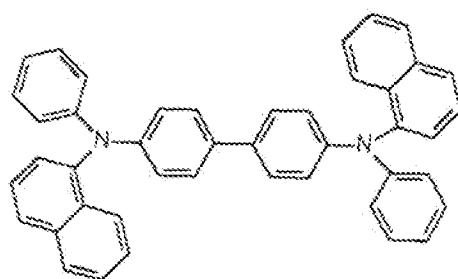
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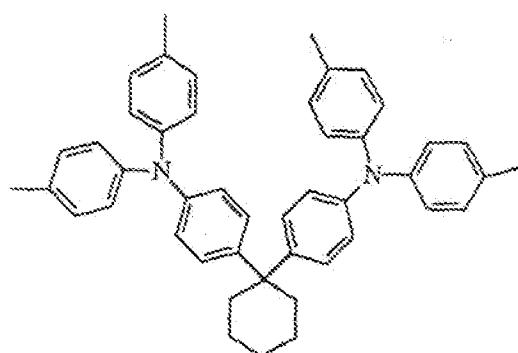
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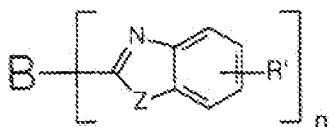


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[0033] The luminescent layer [Layer 314 of Fig. 3] of the organic EL medium comprises of a luminescent or fluorescent material where electroluminescence is produced as a result of electron-hole pair recombination in this region. In the simplest construction, the luminescent layer comprises of a single component, that is a pure material with a high fluorescent efficiency. A well known material is tris (8-quinolinato) Aluminum, (Alq), which produces excellent green electroluminescence. A preferred embodiment of the luminescent layer comprises a multicomponent material consisting of a host material doped with one or more components of fluorescent dyes. Using this method, highly efficient EL devices can be constructed. Simultaneously, the color of the EL devices can be tuned by using fluorescent dyes of different emission wavelengths in a common host material. This dopant scheme has been described in considerable details for EL devices using Alq as the host material by Tang and others [J. Applied Physics, Vol. 65, Pages 3610-3616, 1989; US-A-4,739,292].

[0034] An important relationship for choosing a fluorescent dye as a dopant capable of modifying the hue of light emission when present in a host material is a comparison of their bandgap potential which is defined as the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital of the molecule. For efficient energy transfer from the host to the dopant molecule, a necessary condition is that the bandgap of the dopant is smaller than that of the host material. An advantage of using a blue host such as benzazole is that its bandgap is sufficiently large to effect energy transfer to a range of commonly available fluorescent dyes emitting in the blue. These blue dopants includes coumarins, stilbenes, distyrylstilbenes, derivatives of anthracene, tetracene, perylene, and other conjugated benzenoids. Other dopants for EL emissions at longer wavelengths include coumarins, rhodamines and other green or red emitting fluorescent dyes.

[0035] In the practice of the present invention, the class of organic materials useful in forming the electron-transport layer [Layer 316 of Fig. 3] of the organic EL devices has the molecular formula as follows:



Formula I

wherein:

n is an integer of from 3 to 8;

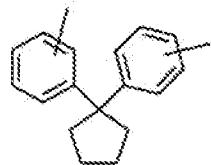
Z is NR or S, and

R and R' are individually hydrogen; alkyl of from 1 to 24 carbon atoms, for example, propyl, t-butyl, heptyl, and the like; aryl or hetero-atom substituted aryl of from 5 to 20 carbon atoms, for example, phenyl and naphthyl, furyl, thiényl; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring;

S is a linkage unit consisting of alkyl, aryl, substituted alkyl, or substituted aryl which conjugately or unconjugately connects the multiple benzazoles together.

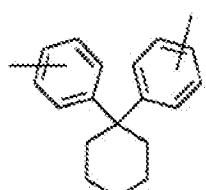
Group 1:

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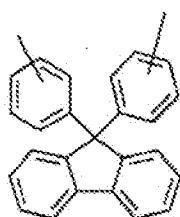
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Group 2:



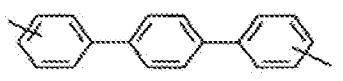
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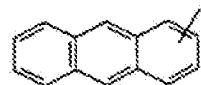
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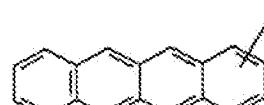




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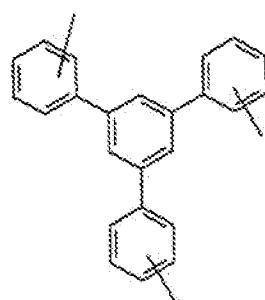


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Group 3:

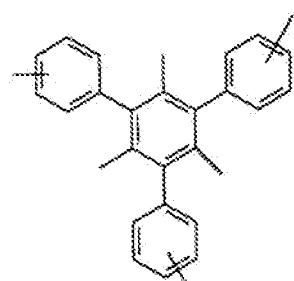
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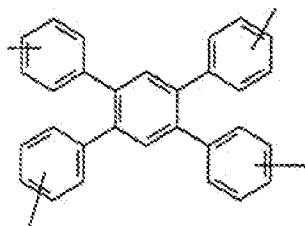
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Group 4:

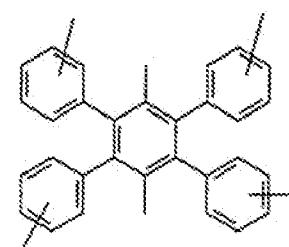
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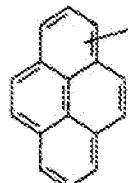


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Group 5:

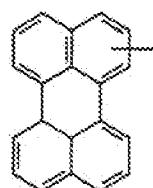
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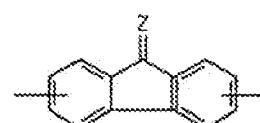


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Group 6:

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in which Z is O or C(CN)₂;

Group 7:

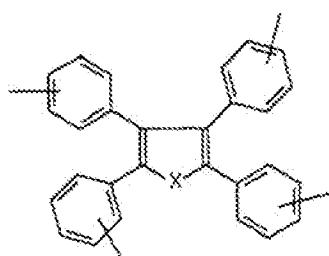
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and

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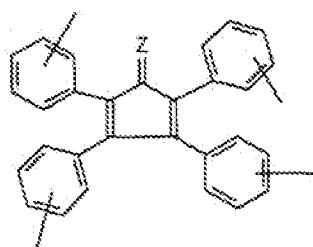
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in which X is O, S, SO₂, CH₂, CHR, CRR', or NR; and R and R' are individually hydrogen; saturated aliphatic of from 1 to 24 carbon atoms, for example, propyl, t-butyl, heptyl, and the like; aryl of from 6 to 20 carbon atoms, for example, phenyl and naphthyl; or halo such as chloro, fluoro, and the like; or R and R' individually comprise the atoms necessary to complete a fused aromatic ring;

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Group 8:

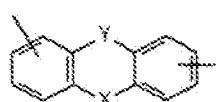
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in which Z is O or C(CN)₂; and

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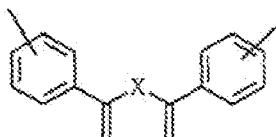
in which X and Y are individually O, S, SO₂, CH₂, CHR, CRR', or NR; and R and R' are individually hydrogen; saturated aliphatic of from 1 to 24 carbon atoms, for example, propyl, t-butyl, heptyl, and the like; aryl of from 6 to 20 carbon atoms, for example, phenyl and naphthyl; or halo such as chloro, fluoro, and the like; or R and

R' individually comprise the atoms necessary to complete a fused aromatic ring;

Group 8:

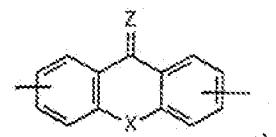
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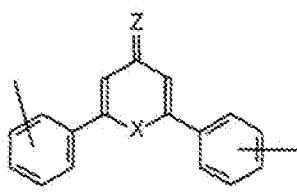
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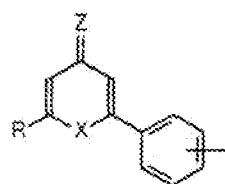
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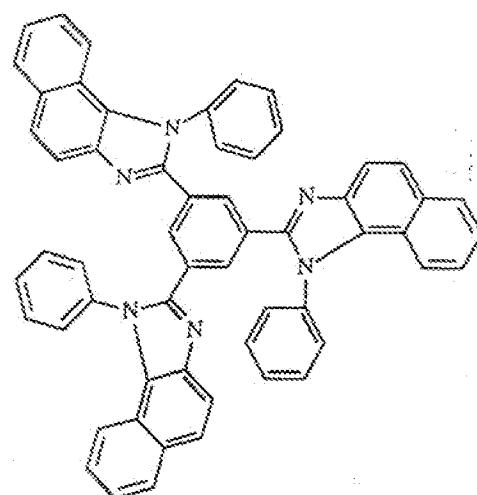
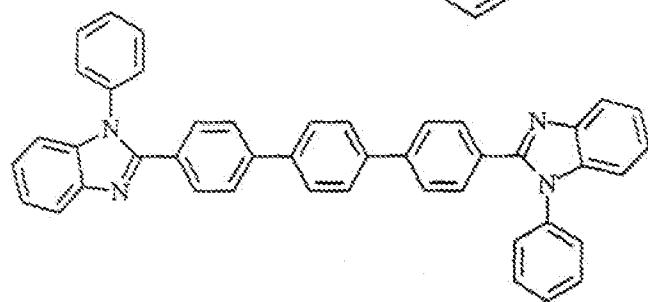
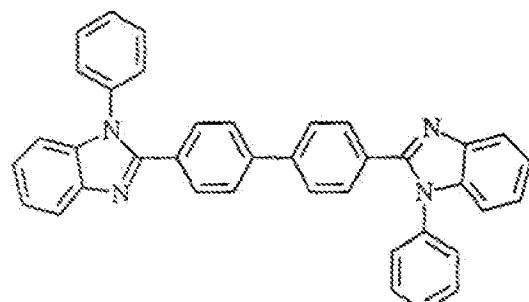
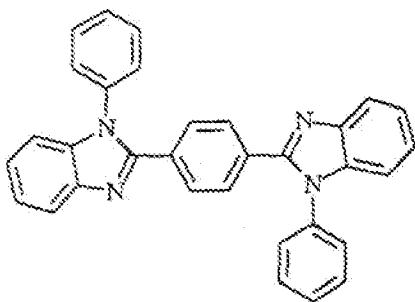


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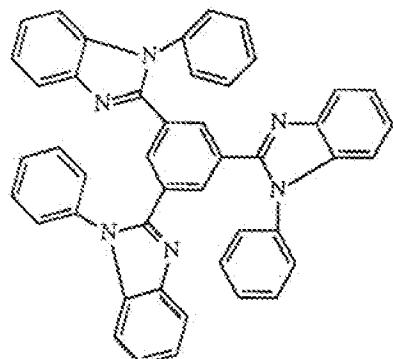
in which Z is O or C(CN)₂; X is O, S, SO₂, CH₂, CR₁R₂, or NR; and R or R' are individually hydrogen; saturated aliphatic of from 1 to 24 carbon atoms, for example, propyl, t-butyl, heptyl, and the like; aryl of from 6 to 20 carbon atoms, for example, phenyl and naphthyl; or halo such as chloro, fluoro, and the like; or R and R' individually comprise the atoms necessary to complete a fused aromatic ring.

[0036] The following molecular structures constitute specific examples of preferred benzazoles satisfying the requirement of the invention:

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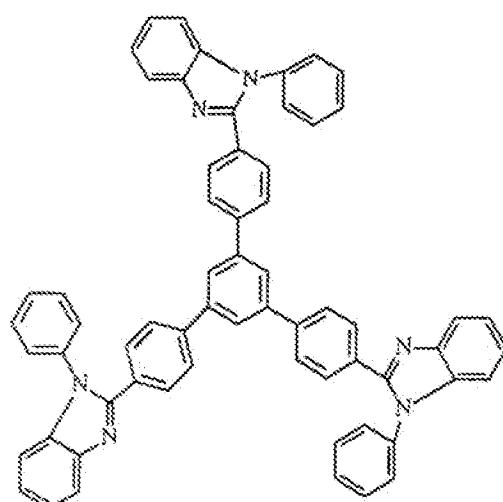
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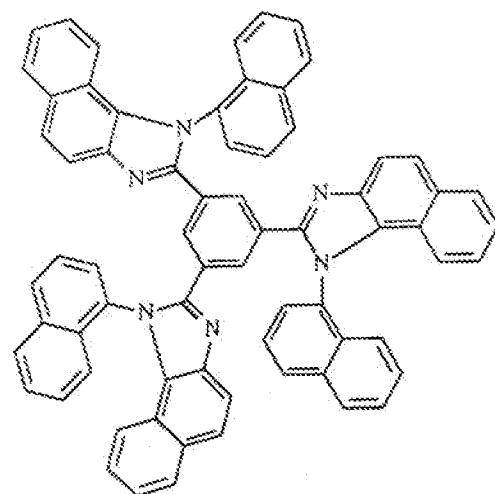
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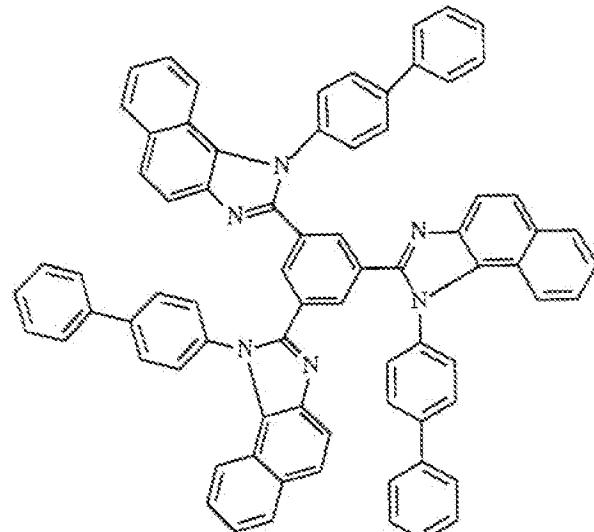
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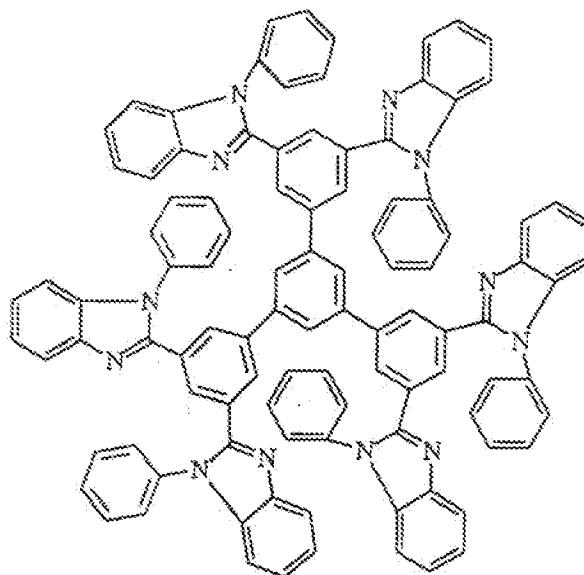
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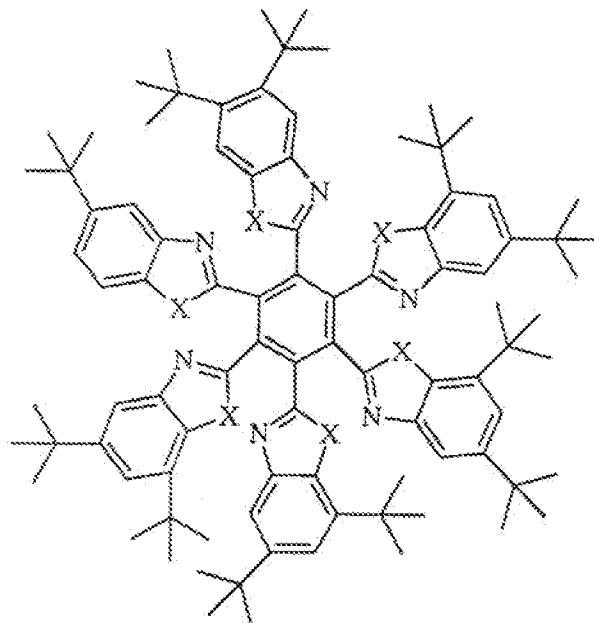
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 $X=S_2$

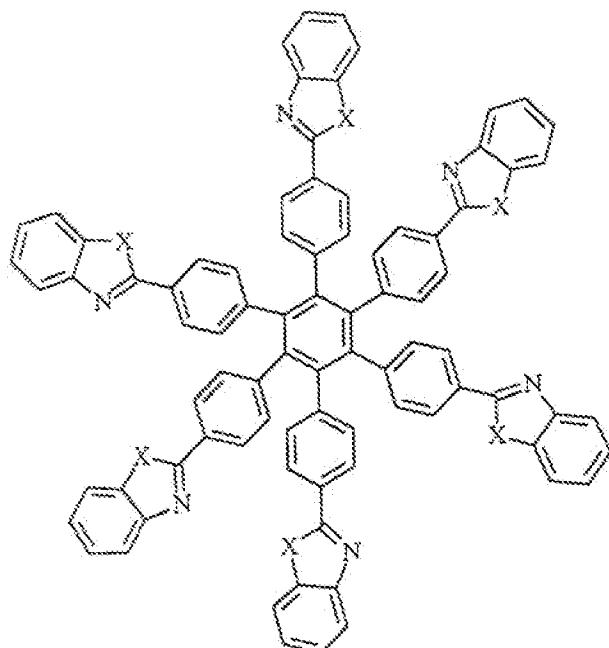
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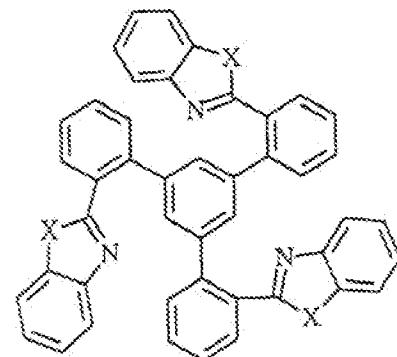
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 $X=S_2$

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X=S, NAr

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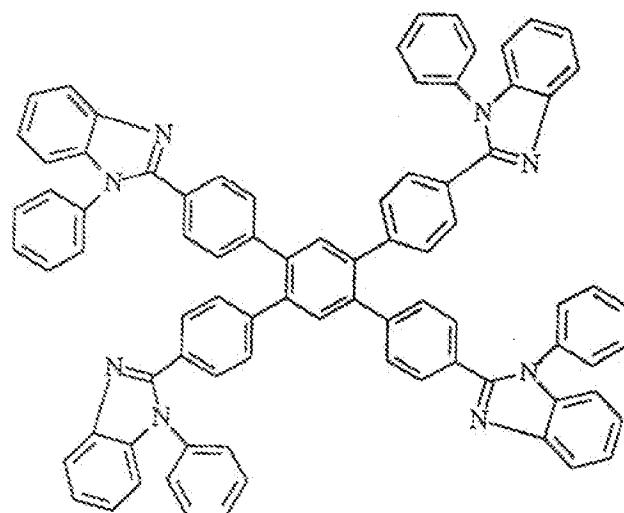
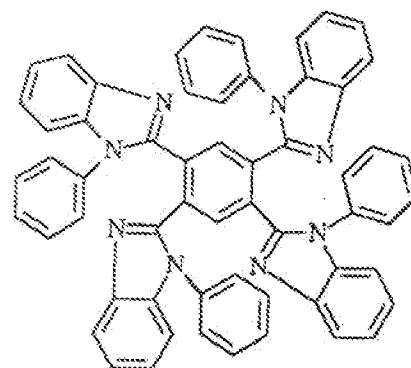
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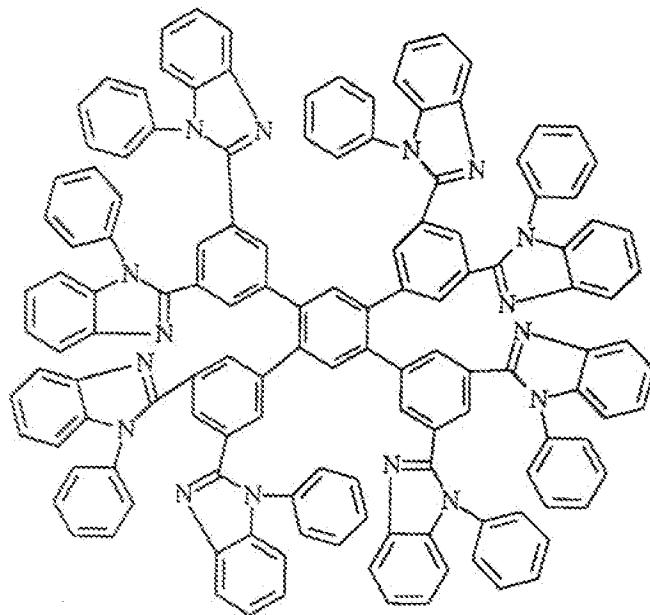
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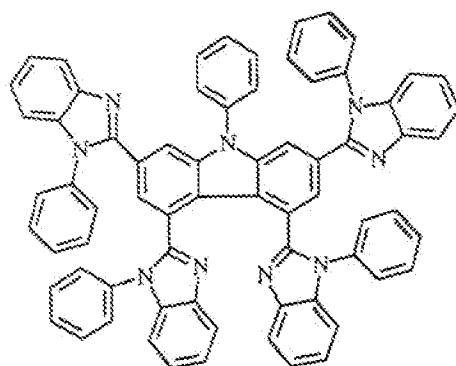
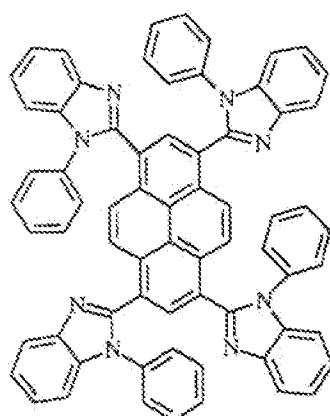
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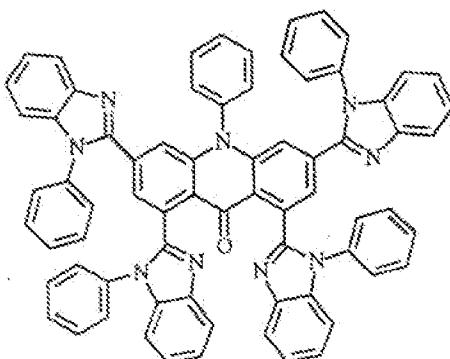
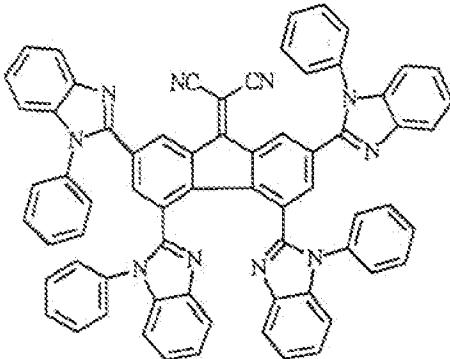
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The electron-transport layer of the organic EL medium preferably should have a high electron mobility. A high mobility material would result in lower voltage drop across the transport layer and therefore a higher efficiency for the EL device. In addition, it is highly desirable for the electron-transport material to have a wide bandgap, that is with an energy gap in excess of 2.00 eV. With a wide bandgap electron-transport material, the EL emission from the luminescent layer which is sandwiched between the hole-transport layer and the electron-transport layer can transmit through the electron-transport layer without attenuation by absorption. More importantly, a wide bandgap transport material would make the energy or charge transfer from the luminescent layer back to the transport layer less favorable, thus confining the light emission primarily in the luminescent layer.

[0037] The preferred materials for the multi-layers of the organic EL medium are each capable of film-forming—that is, capable of being fabricated as a continuous layer having a thickness of less than (500 nm) 5000 Å. A preferred method for forming the organic EL medium is by vacuum vapor deposition. Extremely thin defect-free continuous layers can be formed by this method. Specifically, the individual layer thickness as low as about 50 nm (50 Å) can be constructed while still realizing satisfactory EL device performance. It is generally preferred that the overall thickness of the organic EL medium be at least about 1000 Å (100 nm).

[0038] Other methods for forming thin films in EL devices of this invention include spin-coating from a solution containing the EL material. A combination of spin-coating method and vacuum vapor deposition method is also useful for the fabrication of multi-layer EL devices.

[0039] The anode and cathode of the organic EL device can each take any convenient conventional form. Where it is intended to transmit light from the organic EL device through the anode, this can be conveniently achieved by coating a thin conductive layer onto a light transparent substrate—for example, a transparent or substantially transparent glass plate or plastic film. In one form the organic EL devices of this invention can follow the historical practice of including a light transparent anode formed of tin oxide or indium tin oxide coated on a glass plate, as disclosed by in US-A-3,172,862, US-A-3,173,050, Dresner "Double Injection Electroluminescence in Anthracene", *RCA Review*, Volume 30, pages 322-334, 1969; and US-A-3,710,187 cited above.

[0040] The organic EL devices of this invention can employ a cathode constructed of any metal, including any high or low work function metal, heretofore taught to be useful for this purpose. Unexpected fabrication, performance, and stability advantages have been realized by forming the cathode of a combination of a low work function metal and at

least one other metal. For further disclosure, see US-A-4,885,211.

Examples

5 [0041] The invention and its advantages are further illustrated by the specific examples as follows:

Example 1 - Synthesis of 1,3,5-tris(N-phenyl-N-phenylamino)benzamide

[0042] To a solution of N-phenyl-1,2-phenylenediamine (16.6 g, 0.09 mol) in 100 mL of N-methyl pyrrolidinone was added 1,3,5-benzenetricarbonyl chloride (8.0 g, 0.03 mol) in portion at room temperature under nitrogen. The reaction mixture was stirred at room temperature for two hours then raise the reaction temperature to 50°C for another half hour. After cooling the reaction mixture was poured into 300 ml of cool water with stirring. The resulted precipitates were filtered and washed with water. After drying, the tribenzamide was collected to give 19.5 g. (yield 92%).

15 Example 2 - Synthesis of 2, 2', 2''-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole] (TPBI)

[0043] TPBI was prepared by heating 1,3,5-tris(N-phenyl-N-phenylamino)benzamide in 0.3 atm. nitrogen pressure (3.0×10^4 Pa) at 280 ~295°C for about one hour. The pure TPBI (which can be used directly for cell fabrication) was obtained by sublimation twice at 315°C at 2 Torr pressure (2.5×10^3 Pa)

20 Example 3 - EL device fabrication and performance

[0044] An EL device satisfying the requirements of the invention was constructed in the following manner. The device structure has three organic layers, namely, a hole-injection layer, a hole transport layer and an electron-transport layer.

- a) An indium-tin-oxide (ITO) coated glass substrate was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water, degreased in toluene vapor and exposed to ultraviolet light and ozone for a few minutes.
- b) A hole injection layer of copper phthalocyanine 15 nm (150 Å) was then deposited on top of the ITO coated substrate by evaporation from a tantalum boat.
- c) Onto the copper phthalocyanine layer was deposited a hole transport layer of N,N'-bis-(1-naphthyl)-N,N'-diphenylbenzidine 60nm (600 Å), also by evaporation from a tantalum boat.
- d) An electron-transport layer of TPBI 50 nm (600 Å) was then deposited onto the hole transporting layer.
- e) On top of the TPBI layer was deposited a 2000 Å (200 nm) cathode formed of a 10:1 atomic ratio of Mg and Ag.

35 [0045] The above sequence completed the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.

[0046] The light output from this EL device was 348 cd/m² when it was driven by a current source of 20 mA/cm² and a bias voltage of 7.3 volts. The EL color is blue with 1931 CIE color coordinates of X = 0.153 and Y = 0.157. The EL spectrum shown in Fig. 4 has a peak emission at 460 nm. This EL spectrum indicates that EL emission originates from the electron-transport TPBI layer.

Example 4

[0047] An EL device satisfying the requirements of the invention was constructed in the following manner. The device structure has four organic layers, including, a hole transport layer and a electron-transport layer.

- a) An ITO glass substrate was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water, degreased in toluene vapor and exposed to ultraviolet light and ozone for a few minutes.
- b) A hole injection layer of copper phthalocyanine 15 nm (150 Å) was then deposited on top of the ITO coated substrate by evaporation from a tantalum boat.
- c) A hole transport layer 60 nm (600 Å) of N,N'-bis-(1-naphthyl)-N,N'-diphenylbenzidine was then deposited on top of the ITO glass, also by evaporation from a tantalum boat.
- d) A luminescent layer of Alq 37.5 nm (375 Å) was then deposited onto the hole transport layer.
- e) An electron-transport layer TPBI 37.5 nm (375 Å) was then deposited onto the luminescent layer.
- f) On top of the electron-transport layer was deposited a cathode 200 nm (2000 Å) formed of a 10:1 atomic ratio of Mg and Ag.

[0048] The above sequence completed the deposition of the EL device. The device was then hermetically packaged

in a dry glove box for protection against ambient environment.

[0049] The light output from this EL device was 631 cd/m² when it was driven by a current source of 20 mA/cm² and a bias voltage of 8.9 volts. The EL color is green with 1931 CIE color coordinates of X = 0.316 and Y = 0.557. The EL spectrum has a peak emission at 528 nm.

Example 5

[0050] An EL device satisfying the requirements of the invention was constructed in the following manner. The device structure has four organic layers, including, a hole transport layer and a electron-transport layer.

- a) An ITO glass substrate was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water, degreased in toluene vapor and exposed to ultraviolet light and ozone for a few minutes.
- b) A hole injection layer of copper phthalocyanine 15 nm (150 Å) was then deposited on top of the ITO coated substrate by evaporation from a tantalum boat.
- c) a hole transport layer 60 nm (600 Å) of N,N'-bis-(1-naphthyl)-N,N'-diphenylbenzidine was then deposited on top of the ITO glass, also by evaporation from a tantalum boat.
- d) A luminescent layer of 4,4'-bis-[(2,2-diphenyl)ethenyl]-1,1-biphenyl 30 nm (300 Å) was then deposited onto the hole transport layer.
- e) An electron-transport layer TPBI 20 nm (200 Å) was then deposited onto the luminescent layer.
- f) On top of the electron-transport layer was deposited a cathode 200 nm (2000 Å) formed of a 10:1 atomic ratio of Mg and Ag.

[0051] The above sequence completed the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.

[0052] The light output from this EL device was 537 cd/m² when it was driven by a current source of 20 mA/cm². The EL color is blue with 1931 CIE color coordinates of X = 0.164 and Y = 0.159. The EL spectrum has a peak emission at 460 nm.

Example 6

[0053] An EL device satisfying the requirements of the invention was constructed in the following manner. The device structure has four organic layers, including, a hole transport layer and a electron-transport layer.

- a) An ITO glass substrate was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water, degreased in toluene vapor and exposed to ultraviolet light and ozone for a few minutes.
- b) A hole injection layer of copper phthalocyanine 15 nm (150 Å) was then deposited on top of the ITO coated substrate by evaporation from a tantalum boat.
- c) a hole transport layer 60 nm (600 Å) of N,N'-bis-(1-naphthyl)-N,N'-diphenylbenzidine was then deposited on top of the ITO glass, also by evaporation from a tantalum boat.
- d) A luminescent layer of bis(2-methyl-8-quinolinolato)(2,3-dimethylphenolato)aluminum(III) (B-Alq, 37.5 nm 375 Å) was then deposited onto the hole transport layer.
- e) An electron-transport layer TPBI 37.5 nm (375 Å) was then deposited onto the luminescent layer.
- f) On top of the electron-transport layer was deposited a cathode 200 nm (2000 Å) formed of a 10:1 atomic ratio of Mg and Ag.

[0054] The above sequence completed the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.

[0055] The light output from this EL device was 666 cd/m² when it was driven by a current source of 20 mA/cm². The EL color is blue-green with 1931 CIE color coordinates of X = 0.208 and Y = 0.360. The EL spectrum has a peak emission at 492 nm.

Comparative Example

[0056] An EL devices constructed in a manner similar to Example 6, except that the electron-transport layer is Alq (375Å) instead of TPBI. The luminance output of this EL device was 460 cd/m² when it was driven by a current source of 20 mA/cm². The CIE color co-ordinates are X = 0.214 and Y = 0.373. The EL spectrum has a peak emission at 492 nm. This example illustrates that TBPI as an electron-transport material produces a more efficient EL devices than Alq.

Parts List

[0057]

5 100 EL Device
 102 Substrate
 104 Anode
 106 Cathode
 108 Organic EL medium
 10 110 Hole-transport layer
 112 Electron-transport layer
 114 External power source
 116 Conductor
 118 Conductor
 15 120 Holes
 122 Electrons
 200 EL device
 202 Substrate
 204 Anode
 20 206 Cathode
 208 Organic EL medium
 210 Hole-transport layer
 212 Luminescent layer
 214 Electron-transport layer
 25 300 EL device
 302 Substrate
 304 Anode
 306 Cathode
 308 Organic EL medium
 30 310 Hole-injection layer

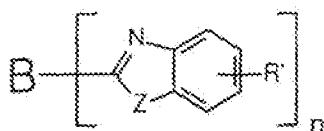
Parts List cont'd

[0058]

35 312 Hole-transport layer
 314 Luminescent layer
 316 Electron-transport layer
 318 Electron-Injection layer
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Claims

45 1. An organic EL device, comprising an anode and a cathode; and at least one electron transporting layer containing
 a compound of benzazoles of the formula:



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Formula I

wherein:

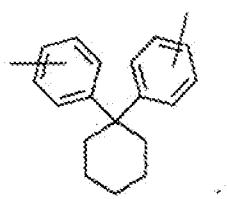
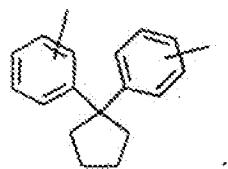
n is an integer of from 3 to 8;

Z is NR or S; and

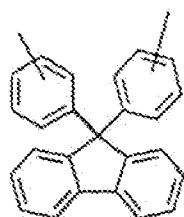
R and R' are individually hydrogen; alkyl of from 1 to 24 carbon atoms, for example, propyl, t-butyl, heptyl, and the like; aryl or hetero-atom substituted aryl of from 5 to 20 carbon atoms, for example, phenyl and naphthyl, furyl, thiienyl, pyridyl, quinolinyl and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring;

B is a linkage unit consisting of alkyl, aryl, substituted alkyl, or substituted aryl which conjugately or unconjugately connects the multiple benzazoles together.

2. An organic EL device as claimed in Claim 1, wherein the linkage unit B consists of:



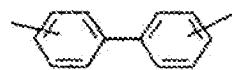
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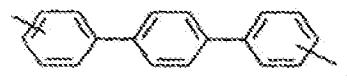
3. An organic EL device as claimed in Claim 1 wherein the linkage unit B consists of:



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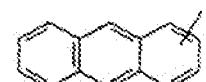
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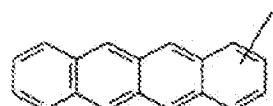
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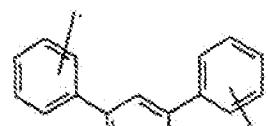
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4. An organic EL device as claimed in Claim 1 wherein the linkage unit B consists of:

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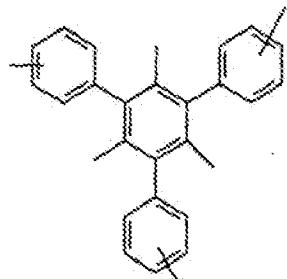
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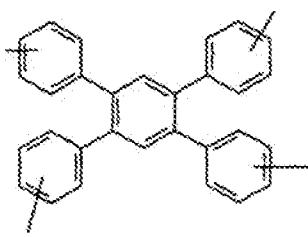
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5. An organic EL device as claimed in Claim 1 wherein the linkage unit B consists of:

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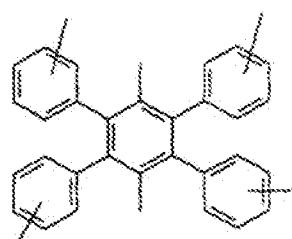


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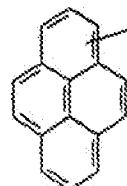
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40 6. An organic EL device as claimed in Claim 1 wherein the linkage unit B consists of:

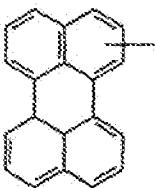
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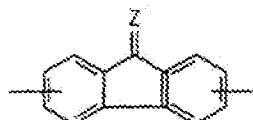


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7. An organic EL device as claimed in Claim 1 wherein the linkage unit B consists of:

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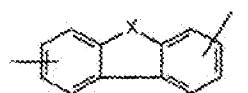


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in which Z is O or C(CN)₂.

8. An organic EL device as claimed in Claim 1 wherein the linkage unit B consists of:

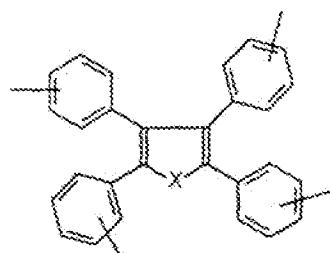
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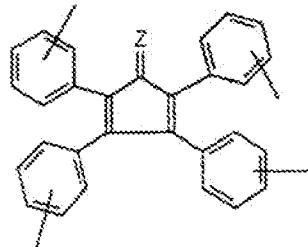
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in which X is O, S, SO₂, CH₂, CHR, CRR', or NR; and R and R' are individually hydrogen; saturated aliphatic of from 1 to 24 carbon atoms, for example, propyl, t-butyl, heptyl, and the like; aryl of from 6 to 20 carbon atoms, for example, phenyl and naphthyl; or halo such as chloro, fluoro, and the like; or R and R' individually comprise the atoms necessary to complete a fused aromatic ring.

9. An organic EL device as claimed in Claim 1 wherein the linkage unit B consists of:

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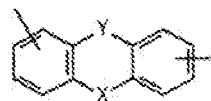
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in which Z is O or C(CN)₂; or

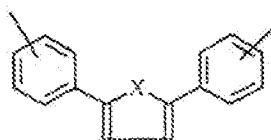
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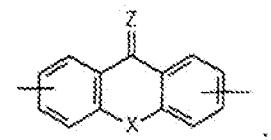
20 in which X and Y are individually O, S, SO₂, CH₂, CHR, CRR', or NR; and R and R' are individually hydrogen; saturated aliphatic of from 1 to 24 carbon atoms, for example, propyl, t-butyl, heptyl, and the like; aryl of from 6 to 20 carbon atoms, for example, phenyl and naphthyl; or halo such as chloro, fluoro, and the like; or R and R' individually comprise the atoms necessary to complete a fused aromatic ring.

25 18. An organic EL device as claimed in Claim 1 wherein the linkage unit B consists of:

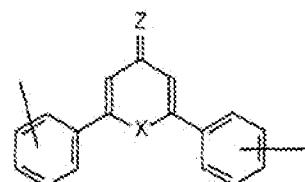
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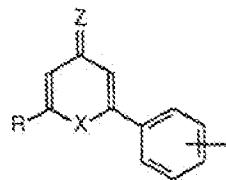


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or

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in which Z is O or C(CN)₂, X is O, S, SO₂, CH₂, CHR, CRR', or NR; and R or R' are individually hydrogen; saturated aliphatic of from 1 to 24 carbon atoms, for example, propyl, 1-butyl, heptyl, and the like; aryl of from 6 to 20 carbon atoms, for example, phenyl and naphthyl; or halo such as chloro, fluoro, and the like; or R and R' individually comprise the atoms necessary to complete a fused aromatic ring.

15 Patentansprüche

1. Organische Elektrolumineszenzvorrichtung mit einer Anode und einer Kathode und mindestens einer Elektronen-transportsschicht, die eine Benzazolverbindung folgender Formel umfasst:

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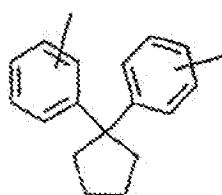
Formel 1

wobei:

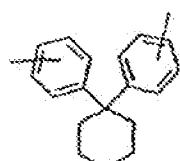
n eine ganze Zahl von 3 bis 8 ist;
 Z ist NR oder S; und
 R und R' sind jeweils Wasserstoff; Alkyl aus 1 bis 24 Kohlenstoffatomen, beispielsweise Propyl, T-Butyl, Heptyl usw.; Aryl oder heteroatomsubstituiertes Aryl aus 5 bis 20 Kohlenstoffatomen, beispielsweise Phenyl und Naphthyl, Furyl, Thienyl, Pyridyl, Quinolinyl und andere heterozyklische Systeme; oder Halogen, wie Chlor, Fluor; oder Atome, die zur Vervollständigung eines kondensierten Benzolrings notwendig sind;
 B ist eine Verkettungseinheit aus Alkyl, Aryl, substituiertem Alkyl oder substituiertem Aryl, welche konjugiert oder unkonjugiert die Vielzahl von Benzazolen miteinander verbindet.

2. Organische Elektrolumineszenzvorrichtung nach Anspruch 1, dadurch gekennzeichnet, dass die Bindungseinheit B besteht aus:

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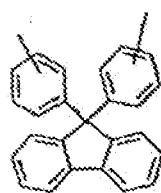


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oder

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3. Organische Elektrolumineszenzvorrichtung nach Anspruch 1, dadurch gekennzeichnet, dass die Bindungsseinheit B besteht aus:

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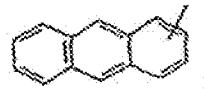
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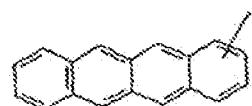
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oder

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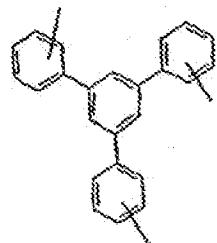


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4. Organische Elektrolumineszenzvorrichtung nach Anspruch 1, dadurch gekennzeichnet, dass die Bindungsseinheit C besteht aus:

heit B besteht aus:

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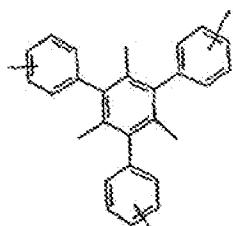


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oder

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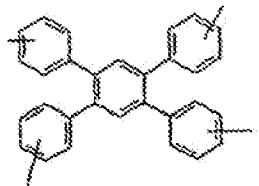


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5. Organische Elektrolumineszenzvorrichtung nach Anspruch 1, dadurch gekennzeichnet, dass die Bindungseinheit B besteht aus:

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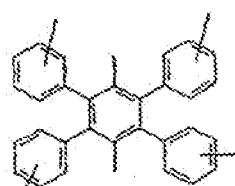


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oder

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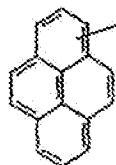
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6. Organische Elektrolumineszenzvorrichtung nach Anspruch 1, dadurch gekennzeichnet, dass die Bindungseinheit B besteht aus:

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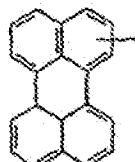


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oder

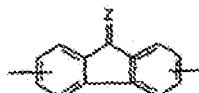
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7. Organische Elektrolumineszenzvorrichtung nach Anspruch 1, dadurch gekennzeichnet, dass die Bindungseinheit B besteht aus:

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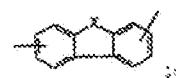


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wobei Z O ist oder $\text{C}(\text{CN})_2$.

- 35 8. Organische Elektrolumineszenzvorrichtung nach Anspruch 1, dadurch gekennzeichnet, dass die Bindungseinheit B besteht aus:

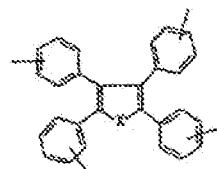
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45

oder

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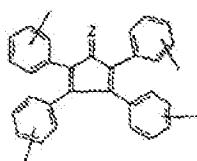


55

- wobei X ist O, S, SO_2 , CH_2 , CHR , CRR' oder NR ; und R und R' sind jeweils Wasserstoff, gesättigte Aliphaten aus 1 bis 24 Kohlenstoffatomen, beispielsweise Propyl, T-Butyl, Heptyl usw.; Aryl aus 6 bis 20 Kohlenstoffatomen, beispielsweise Phenyl und Naphthyl; oder Halogene, wie Chlor, Fluor usw.; oder R und R' umfassen jeweils Atome, die zur Vervollständigung eines kondensierten Benzolrings notwendig sind.

9. Organische Elektrolumineszenzvorrichtung nach Anspruch 1, dadurch gekennzeichnet, dass die Bindungseinheit B besteht aus:

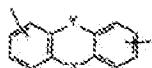
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wobei Z O ist oder $\text{C}(\text{CN})_2$; oder

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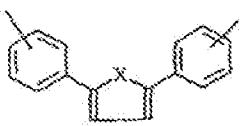
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wobei X und Y jeweils O, S, SO_2 , CH_2 , CHR , $\text{CR}'\text{R}'$ oder NR sind, und R und R' sind jeweils Wasserstoff; gesättigte Aliphaten aus 1 bis 24 Kohlenstoffatomen, beispielsweise Propyl, T-Buyl, Heptyl usw.; Aryl aus 6 bis 20 Kohlenstoffatomen, beispielsweise Phenyl und Naphthyl; oder Halogene, wie Chlor, Fluor usw.; oder R und R' umfassen jeweils die Atome, die zur Vervollständigung eines kondensierten Benzolrings notwendig sind.

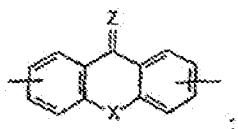
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10. Organische Elektrolumineszenzvorrichtung nach Anspruch 1, dadurch gekennzeichnet, dass die Bindungseinheit B besteht aus:

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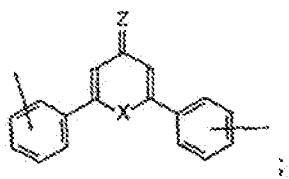


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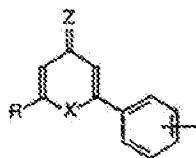


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oder

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wobei Z ist O oder C(CN)₂, X ist O, S, SO₂, CH₂, CHR, CRR', oder NR und R oder R' sind einzeln Wasserstoff; gesättigte Aliphaten aus 1 bis 24 Kohlenstoffatomen, beispielsweise Propyl, T-Butyl, Heptyl usw.; Aryl aus 6 bis 20 Kohlenstoffatomen, beispielsweise Phenyl und Naphthyl; oder Halogene, wie Chlor, Fluor usw.; oder R und R' umfassen jeweils die Atome, die zur Vervollständigung eines kondensierten Benzolrings notwendig sind.

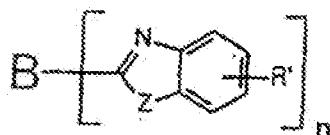
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Revendications

1. Dispositif organique EL, comprenant une anode et une cathode, et au moins une couche transporteuse d'électrons contenant un composé de benzazoles ayant la formule :

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Formule I

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dans laquelle :

n est un nombre entier compris entre 3 et 8 ;

Z représente NR ou S ; et

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R et R' représentent séparément un hydrogène ; un groupe alkyle ayant 1 à 24 atomes de carbone, par exemple un groupe propyle, t-butyle, heptyle et groupes similaires ; un groupe aryle ou un groupe aryle substitué par un hétéroatome ayant 5 à 20 atomes de carbone, par exemple un groupe phényle, naphthyle, furyle, thiényle, pyridyle, quinolinyle et autres systèmes hétérocycliques ; halo tel que chloro ou fluoro ; ou les atomes nécessaires pour compléter un noyau aromatique condensé ;

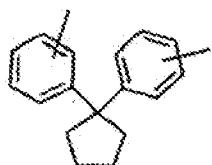
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B est un élément de liaison constitué d'un groupe alkyle, aryle, alkyle substitué ou aryle substitué qui, de façon conjuguée ou non, relie les multiples groupes benzazoles.

2. Dispositif organique EL selon la revendication 1, dans lequel l'élément de liaison B est constitué de :

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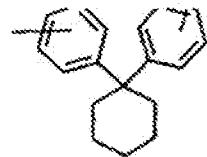
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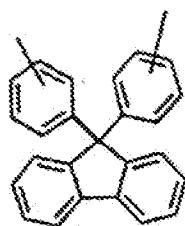
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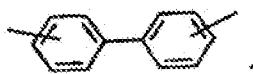


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25 3. Dispositif organique E1 selon la revendication 1, dans lequel l'élément de liaison B est constitué de :

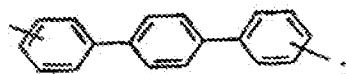


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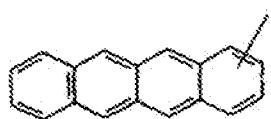
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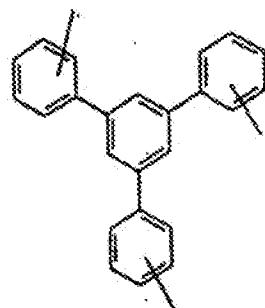
10 OU

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20 4. Dispositif organique EL selon la revendication 1, dans lequel l'élément de liaison B est constitué de :

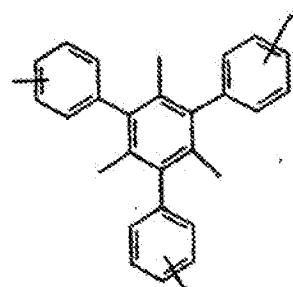
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30

35 OU

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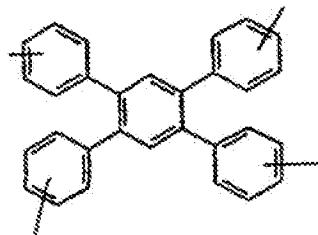


45

50 5. Dispositif organique EL selon la revendication 1, dans lequel l'élément de liaison B est constitué de :

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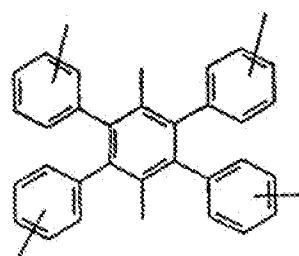
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OU

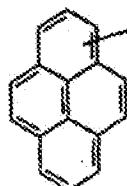
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25 6. Dispositif organique EL selon la revendication 1, dans lequel l'élément de liaison B est constitué de :

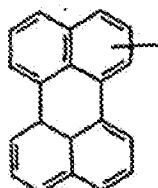
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OU

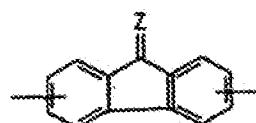
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50 7. Dispositif organique EL selon la revendication 1, dans lequel l'élément de liaison B est constitué de :

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dans laquelle Z représente O ou C(CN)₂.

8. Dispositif organique EL selon la revendication 1, dans lequel l'élément de liaison B est constitué de :

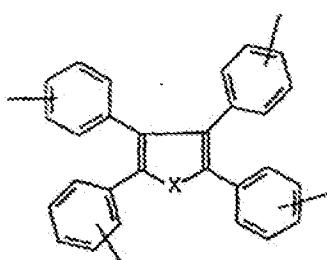
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OU

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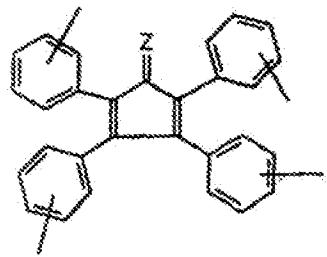
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dans lesquelles X représente O, S, SO₂, CH₂, CHR, CRR' ou NR ; et R et R' représentent séparément un hydrogène ; un groupe aliphatique saturé ayant 1 à 24 atomes de carbone, par exemple un groupe propyle, t-butyle, heptyle et groupes similaires ; un groupe aryle ayant 6 à 20 atomes de carbone, par exemple un groupe phényle ou naphtyle ; halo tel que chloro, fluoro et similaires ; ou R et R' comprennent séparément les atomes nécessaires pour compléter un noyau aromatique condensé.

9. Dispositif organique EL selon la revendication 1, dans lequel l'élément de liaison B est constitué de :

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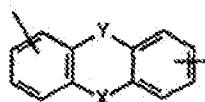


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dans laquelle Z représente O ou C(CN)₂ ; ou

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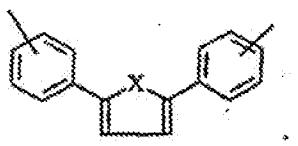


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dans laquelle X et Y représentent séparément O, S, SO₂, CH₂, CHR, CRR' ou NR ; et R et R' représentent séparément un hydrogène ; un groupe aliphatique saturé ayant 1 à 24 atomes de carbone, par exemple un groupe propyle, t-butyle, heptyle et groupes similaires ; un groupe aryle ayant 6 à 20 atomes de carbone, par exemple un groupe phényle ou naphtyle ; halo tel que chloro, fluoro et similaires ; ou R et R' comprennent séparément les atomes nécessaires pour compléter un noyau aromatique condensé.

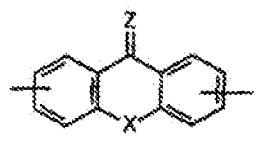
10. Dispositif organique E1, selon la revendication 1, dans lequel l'élément de liaison B est constitué de :

5



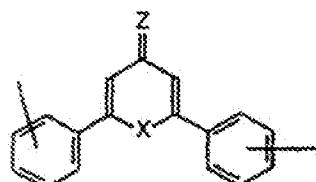
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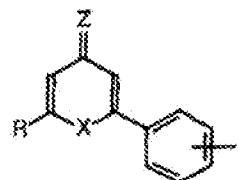
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OU

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dans lesquelles Z représente O ou C(CN)₂ ; X représente O, S, SO₂, CH₂, CHR, CRR' ou NR ; et R et R' représentent séparément un hydrogène ; un groupe aliphatic saturé ayant 1 à 24 atomes de carbone, par exemple un groupe propyle, t-butyle, heptyle et groupes similaires ; un groupe aryle ayant 6 à 20 atomes de carbone, par exemple un groupe phényle ou naphtyle ; halo tel que chloro, fluoro et similaires ; ou R et R' comprennent séparément les atomes nécessaires pour compléter un noyau aromatique condensé.

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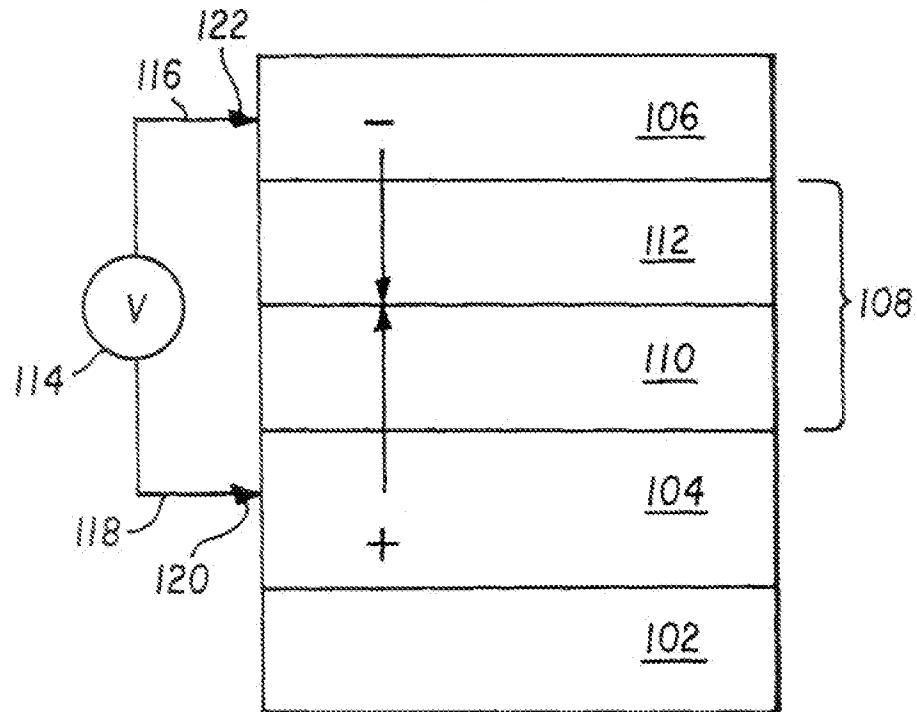


FIG. 1

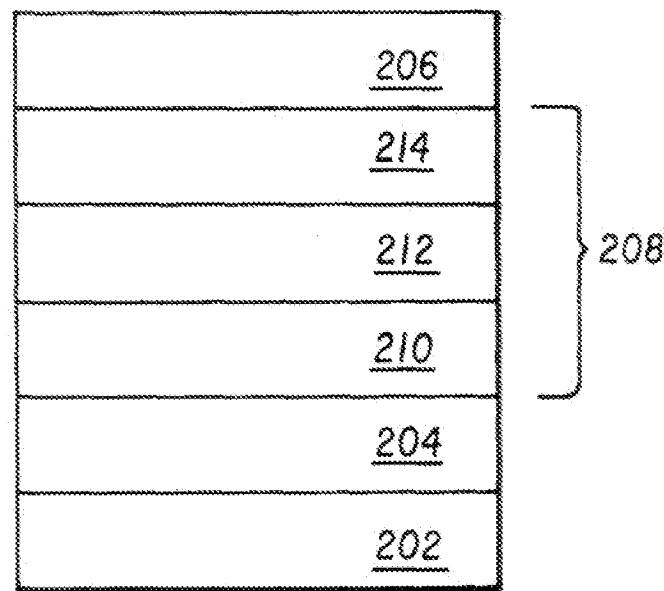


FIG. 2

<u>306</u>
<u>318</u>
<u>316</u>
<u>314</u>
<u>312</u>
<u>310</u>
<u>304</u>
<u>302</u>

> 308

FIG. 3

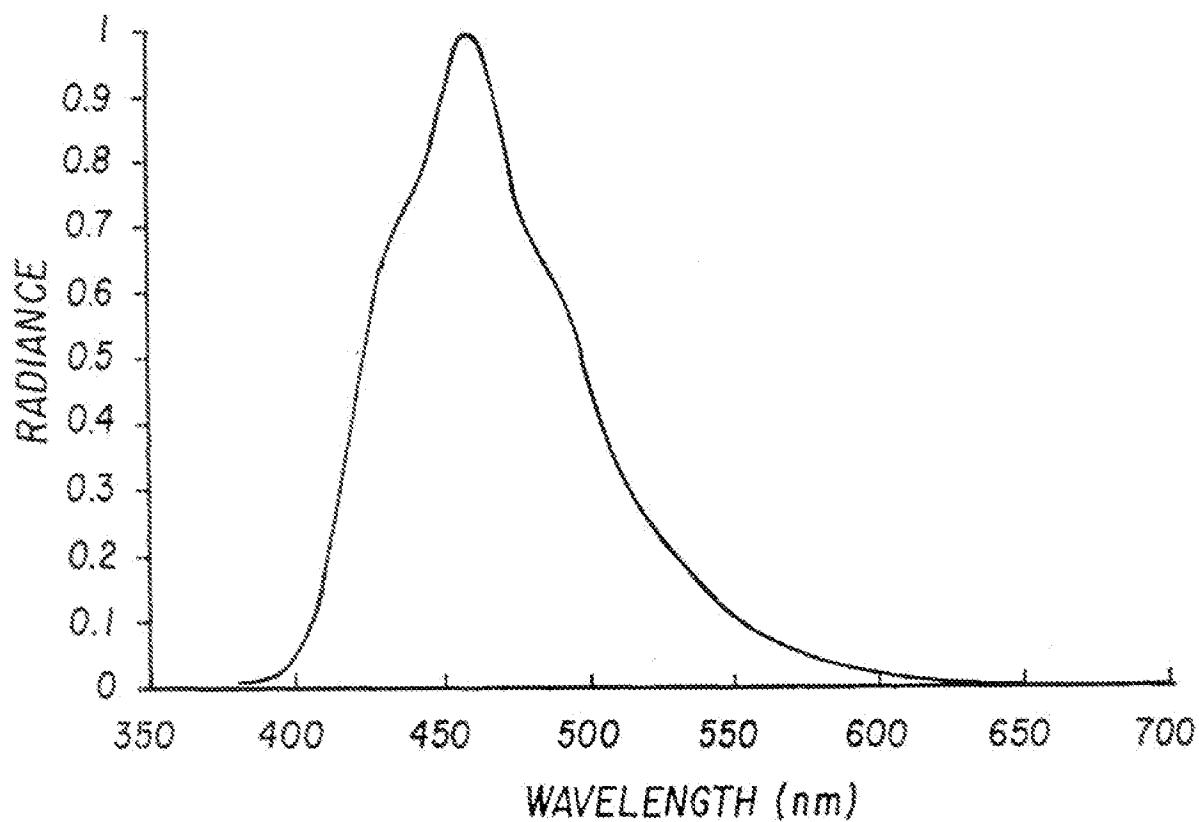


FIG. 4